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## (54) PRODUCTION OF POLYGLYCERYL FATTY ACID ESTER

### (57)Abstract:

PURPOSE: To obtain a surfactant capable of producing perfect dissolution products and stable emulsions in the fields of foods, cosmetics, medicines and other industries.

CONSTITUTION: The method for producing the polyglyceryl fatty acid ester comprises the first process for obtaining a polyglycerol by removing the low molecular reaction products of the polyglycerol with a liquid chromatography using a column filled with the alkaline earth metal salt of a gel type ion exchange resin having a polystyrene skeleton having a cross-linking degree of 8-12%, and the second process containing the esterification reaction of the polyglycerol with a fatty acid. The method is suitable for producing perfect dissolution products and stable emulsions, and enables to produce products which have not been produced.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] The manufacture approach of the polyglyceryl fatty acid ester obtained according to the 1st process which removes the low-molecular reactant of a polyglycerin reactant and obtains polyglycerin with the liquid chromatography using the column filled up with the alkaline-earth-metal salt of the gel mold cation exchange resin which has the polystyrene frame which has 12% or less of degree of cross linking more greatly than 8%, and the 2nd process including esterification with the fatty acid following it [claim 2] The manufacture approach of the polyglyceryl fatty acid ester according to claim 1 characterized by removing the low-molecular reactant of a polyglycerin reactant with the false moving-bed mold liquid chromatography using the column filled up with the alkaline-earth-metal salt of the gel mold cation exchange resin which has the polystyrene frame which has 12% or less of degree of cross linking more greatly than 8%.

[Claim 3] The manufacture approach of polyglyceryl fatty acid ester according to claim 1 to 2 that a polyglycerin reactant uses the partial alcoholate of a glycerol or a glycerol polymer, and halogenation HIDORIN as a raw material, and it is characterized by being the polyglycerin reactant obtained by the dehalogenation alkali-metal salt reaction.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Industrial Application] The polyglyceryl fatty acid ester from which this invention is obtained by this invention about the manufacture approach of the high polyglyceryl fatty acid ester of the capacity to reduce surface tension can be used as a surfactant of a food additive, the object for cosmetics, the object for physic, and industrial use for the purpose, such as emulsification, solubilization, distribution, washing, corrosion prevention, lubrication, electrification prevention, and wetting.

#### [0002]

[Description of the Prior Art] Food-grade surfactants, such as a nonionic surface active agent of ethylene oxide systems, such as various compounds, for example, polyoxyethylene alkyl ether, polyoxyethylene polyhydric-alcohol fatty acid ester, and polyoxyethylene alkyl phenyl ether, a sorbitan fatty acid ester, sucrose fatty acid ester, and polyglyceryl fatty acid ester (polyglycerin condensation ricinoleic-acid ester is included), are conventionally known as emulsification or a solubilizing agent. Since polyglyceryl fatty acid ester can acquire the safety to the body and an environment, and the presentation of varieties also in it and versatility is high, it is the most useful surfactant. The polyglyceryl fatty acid ester used as a raw material of polyglyceryl fatty acid ester or polyglycerin condensation ricinoleic-acid ester was manufactured by carrying out an esterification reaction, using as a raw material the polyglycerin and the fatty acid which carried out the polymerization of the glycerol conventionally under existence of alkali catalysts, such as caustic alkali of sodium, and a high temperature service, and were decolorized [ were deodorized and ] and obtained. Moreover, the polyglycerin which refines the reactant obtained by carrying out and carrying out chemosynthesis of epichlorohydrin, glycidol, a glycerol or polyglycerin, epichlorohydrin, a mono-chlorohydrin, the dichlorohydrin, or the glycidol to a raw material by distillation, decolorization, deodorization, ion-exchange-resin processing, etc. remaining as it is or if needed, and is obtained was used as the raw material, and it esterified, and was manufactured.

#### [0003]

[Problem(s) to be Solved by the Invention] The polyglycerin which is circulating in these commercial scenes is called tetramer polyglycerin, hexamer polyglycerin, and 10 \*\*\*\* polyglycerin by the polymerization degree of the average calculated from the hydroxyl value. However, it is the mixture of the various glycerol polymerization objects from polymerization degree 1 to ten or more in fact. Generally, in these polyglycerin and a fatty acid, when compounding ester by the esterification reaction, the reactivity differs and the polyglycerin of low polymerization degree is alternatively esterified by the polymerization degree of a glycerol. Consequently, the ester obtained serves as mixture of the polyglyceryl fatty acid ester with an ester bond with many fatty acids of low polymerization degree, and unreacted high-polymer polyglycerin without an ester bond from a target. Therefore, they were the emulsification which it originally has, and the thing which cannot demonstrate the solubilization force. For example, when useful matter called lipophilicity coloring matter, such as a vitamin of lipophilicity, such as vitamin E, and carotene, was manufactured as a drink, in the existing food-grade surfactant, transparency solubilization could not be carried out and a product with sufficient preservation stability

was not able to be manufactured. Moreover, in case drugs and cosmetics are manufactured, other surface active agents, for example, polyoxyethylene sorbitan ester, it can be used, but when manufacturing useful matter called lipophilicity coloring matter, such as a vitamin of lipophilicity, such as vitamin E, and carotene, as a drink, since there is not sufficient solubilization capacity if independent, assistants, such as ethanol, are required. Therefore, if it drinks in a large quantity, it will be in an inebriation condition and, especially in the case of the youth, has become a social problem.

[0004] Furthermore, although the polyoxyethylene derivative is used as an emulsifier of a hydrophilic property in the cosmetics industry, a problem is in safeties, such as skin irritation, and although the substitute is called for, conventional polyglyceryl fatty acid ester and sucrose fatty acid ester of engine performance are inadequate, and cannot be substituted. Although the approach of manufacturing high-definition polyglyceryl fatty acid ester using a metal oxide catalyst is indicated in JP,4-145046,A, although an esterolysis and coloring improve, since especially the molecular weight distribution of polyglycerin are uncontrollable by this approach, surface activity capacity of ester [ especially ] obtained does not improve. Although the approach of using and manufacturing lipase is indicated in JP,61-187795,A, JP,61-257191,A, JP,61-257191,A, and JP,3-151885,A in case polyglycerin is esterified, surface activity capacity of this approach does not improve. In JP,63-23837,A and JP,3-81252,A, after esterifying, it has tried to solvent judgment will remove unreacted polyglycerin and improve surface activity capacity, but by this approach, a process becomes complicated, and since yield is low, practical use cannot be presented.

[0005] By carrying out chromatography separation using the strongly acidic cation exchange resin of the gel mold which has the polystyrene frame of 5 - 8% of degrees of cross linking in JP,5-310625,A, furthermore, polyglycerin, Although the approach of separating the polyglycerin constituent manufactured by the approach of carrying out the polymerization especially of the glycerol at an elevated temperature under an alkali catalyst is indicated Resultant slack polyglycerin With the degree of cross linking 6 or about eight ion exchange resin generally conventionally used since the acid which makes the origin the acrolein Mr. matter which carries out a byproduction is included so much during the polyglycerin reaction manufactured by the approach of carrying out the polymerization especially of the glycerol at an elevated temperature under an alkali catalyst, swelling of resin, Contraction was large, and it was divided simply and had the fault referred to as being unable to attain the most important long term stability for industrial production.

[0006]

[Means for Solving the Problem] this invention persons resulted in this invention wholeheartedly in view of the above-mentioned point as a result of research. That is, this invention relates to the manufacture approach of the polyglyceryl fatty acid ester obtained according to the 1st process which removes the low-molecular reactant of a polyglycerin reactant with the liquid chromatography using the column filled up with the alkaline-earth-metal salt of the gel mold cation exchange resin which has the polystyrene frame which has 12% or less of degree of cross linking more greatly than 8%, and obtains polyglycerin, and the 2nd process including esterification with the fatty acid following it. This invention is explained to a detail below. In case the surfactant said to this invention mixes the oleophilic matter and the hydrophilic matter, it is the matter added for the purpose of stabilization, and it has strong surface activity ability. These matter has both an oleophilic functional group and the functional group of a hydrophilic property in the intramolecular, and reduces the surface tension of water to it. The polyglycerin as used in the field of this invention is matter which has a hydroxyl group and ether linkage in the intramolecular obtained by carrying out dehydration condensation of the glycerol, and does not have other functional groups, and points out all the things that have equivalent structure regardless of how of a raw material process.

[0007] The polyglycerin reactant as used in the field of this invention heats a glycerol under ordinary pressure or reduced pressure under an alkali catalyst, and is obtained. Gases, such as nitrogen and a steam, are led for the purpose of use. Remove a component with a stinking low-boiling point etc., or Ion components, such as a catalyst used by ion exchange resin, ion exchange membrane, etc., are removed, or using adsorbents, such as activated carbon, reduction processing is carried out by hydrogenation etc.

and it is refined [ \*\*\*\* / removing a color component and a smell component ]. Moreover, polyglycerin can be obtained even if it compounds and refines them, using glycidol, epichlorohydrin, a mono-chlorohydrin, etc. as a raw material. Furthermore, halogenation HIDORIN, such as the partial alcoholate and dichlorohydrin of a glycerol or its polymer, and mono-chlorohydrin, can be used as a raw material, and it can obtain by the dehalogenation alkali-metal salt reaction. For example, it will become triglycerol and salt if it reacts in two mols of mono-alkoxy glycerol, and one mol of dichlorohydrin. However, by this system, it is desirable to become hyperviscosity very much, and to add a solvent in fact, since compatibility is bad. A glycerol or its polymer of the solvent to be used is more desirable than the simplicity of a purification process. Furthermore, they are a glycerol and diglycerol preferably. Liquid chromatography processing of a back process can remove these solvents easily, and they can be again used as a raw material as occasion demands. Moreover, if in charge of a reaction, it is the purpose which presses down generating of the by-product by the random reaction, and it is desirable to operate it at low temperature as much as possible. 150 degrees C or less of desirable conditions are 130 degrees C or less still more preferably.

[0008] Thus, the obtained polyglycerin reactant also contains very a small amount of more nearly high-polymer polyglycerin which carries out a byproduction as a principal component, including the glycerol used as a solvent or its polymerization object, and a theoretical reactant. Since distribution of molecular weight is narrow compared with the polyglycerin reactant obtained by the usual approach, the polyglycerin reactant which uses the partial alcoholate and halogenation HIDORIN of a glycerol or its polymer as a raw material among these polyglycerin reactants, and is obtained by the dehalogenation alkali-metal salt reaction is the most desirable. Conventionally, if dehydration condensation of the glycerol is carried out, paying attention to two mols of hydroxyl groups of intramolecular changing into one mol of ether linkage, it will be understood as the polymerization degree of polyglycerin as what calculated the polymerization degree of the average by having measured the hydroxyl value by the criteria fats and fatty oils test. In case low-molecular to a macromolecule had large molecular weight distribution and the polyglycerin with which this is conventionally supplied to the commercial scene expressed a presentation numerically, it was complicated, and it was because there was no knowledge which observes molecular weight distribution and the surface activity capacity of the ester obtained so that this invention may describe. However, in having used the measuring method of such polymerization degree, when considering the property of the polyglyceryl fatty acid ester obtained from these polyglycerin, it is unsuitable. Therefore, the degree of polymerization of the polyglycerin in this invention shall perform a separation quantum by the GC method (gas chromatography) polyglycerin derivatives, such as trimethylsilylation or acetylation, nothing, and on it, and shall calculate it in an area method.

[0009] Analysis by the GC method can be easily carried out, if temperature up analysis for 10-degree-C/is performed to 100 degrees C - 250 degrees C using fuze DOSHIRIKA capillary tube tubing to which the chemical bond of the low polar liquid phase, such as methyl silicone, was carried out. Moreover, identification of the peak on gas chromatogram can introduce a gas chromatograph into the double-focusing mass spectrograph, it can be ionized by approaches, such as chemical eye demon ZESHON, and it can measure it, and can be easily performed by calculating the molecular weight of the peak on . gas chromatogram from the molecular weight of the parent ion, and next, searching for the polymerization degree of a glycerol from a chemical formula further. The liquid chromatography said to this invention may be equipment which is made to pass a raw material and is separated using the difference of the distribution coefficient among two phases of the solid particulate which coated the front face with the solid particulate or solution layer with which the column was filled up, and an outflow solvent, and may be liquid chromatography of what kind of well-known method. For example, the raw material and outflow solvent of the specified quantity are supplied to continuation or an intermittence target at a predetermined column, respectively to timing fixed in the single column method and 2-16 columns which supply the constant rate of a raw material to the column which filled the outflow solvent, and supply an outflow solvent after that, and continuation, the false moving-bed mold method extracted intermittently, or its advanced type can use the effluent of the specified quantity from

a predetermined column to fixed timing.

[0010] The solid particulate with which the column used for the liquid chromatography used for this invention was filled up is ion-exchange resin, and is gel mold cation exchange resin which has a polystyrene frame in detail. Depending on the case, the suspension polymerization of this cation exchange resin is carried out, using 1, 2, and 4-trivinylbenzene, 1, 3, and 5-trivinylbenzene, etc. as a cross linking agent, then, it is processed with concentrated sulfuric acid, a chlorosulfonic acid, or a sulfuric anhydride, using a divinylbenzene as a cross linking agent, using styrene as a main raw material, introduces a functional group, and is obtained by making the water solution of an alkaline-earth-metal salt contact. In this case, a degree of cross linking is determined by the blending ratio of coal of a cross linking agent. For example, if the suspension polymerization of the divinylbenzene 10 section is blended and carried out to the styrene 90 section, the resin of a degree of cross linking 10 will generate, or if the suspension polymerization of the divinylbenzene 12 section is blended and carried out to the styrene 88 section, the resin of a degree of cross linking 12 will generate. In this case, when a cross linking agent is made to increase, in the case of a suspension polymerization, many chemical bonds generate in three dimensions, and physical reinforcement and chemistry reinforcement become large. When using for the purpose of this invention, as mentioned above, swelling of resin and contraction are large because of the acid which carries out a byproduction during a reaction, and it is easy to generate the phenomenon in which resin breaks. Therefore, it is difficult for it to be stability for a long period of time, and the degree of cross linking exceeding 8 is required of the degree of cross linking 6 usually used or the resin of 8. However, if the resin which has a bigger degree of cross linking than 12 is used just because it asks for reinforcement, since separability ability falls very much, it is unsuitable. Moreover, the object which has one to 2 meq/ml preferably 0.5 to 3 meq/ml as exchange capacity in installation of a functional group is good.

[0011] The alkaline-earth-metal salts used for this invention are calcium, magnesium, etc., and the chloride is usually used. In this case, as for the selected salt, considering as one kind is desirable. If it uses, other metal ions, for example, alkali-metal ion, too required reinforcement cannot be obtained but stable use is difficult for a result long period of time. It is desirable to carry out enough until contact of resin and alkaline-earth-metal salting in liquid reaches a balance. After filling up a column with the above ion exchange resin and adding the water solution of a polyglycerin reactant, if eluted using water, the water solution of the polyglycerin in which elution is carried out to sequence by polymerization degree and which has the target distribution of polymerization degree with it can be obtained. In this case, acid, such as salts, such as a sodium chloride, sodium acetate, a sodium sulfate, sodium phosphate, and a sodium citrate, or an acetic acid, phosphoric acid, and a citric acid, may be added in the water to elute. Or the way acid chloride of a way acid potassium etc. may be used again. Under the present circumstances, although the thing of any distribution of polymerization degree can be isolated preparatively according to conditions, in order to perform suitable esterification in a next esterification reaction, the narrow thing of the width of distribution is desirable, and it is desirable to isolate with a polymerization degree of three or more polyglycerin preparatively. It is still more desirable to isolate preparatively three or more polymerization degree and ten or less polyglycerin. It is isolating preparatively four or more polymerization degree and ten or less polyglycerin most preferably. the law after heating the water solution of the polyglycerin obtained in this way under reduced pressure and removing water -- esterification with a fatty acid can be performed according to a method, and target polyglyceryl fatty acid ester can be obtained.

[0012] The fatty acid said to this invention is especially the generic name of the matter which contains the carboxylic acid which hydrolyzes the fats and oils extracted from natural animals and plants, and dissociates, or refines, without dissociating, and is obtained as a functional group, and it does not limit. The fatty acid of this invention may be a polymerization fatty acid obtained by carrying out the heating polymerization of the condensation fatty acid obtained by using petroleum etc. as a raw material and carrying out condensation polymerization of what you may be the fatty acid which compounds chemically and is obtained, and hydrogenation etc. carried out these fatty acids, and returned, and the fatty acid containing a hydroxyl group, and the fatty acid which has an unsaturated bond. The mixture of

oleic acid, isostearic acid, a palmitic acid, a lauric acid, a capric acid, a caprylic acid, a ricinoleic acid, 12-hydroxy stearic acid, a condensation ricinoleic acid, condensation 12-hydroxy stearic acid, a caproic acid, a heptyl acid, a nonyl acid, undecanoic acid, a myristic acid, stearic acid, palmitoleic acid, behenic acid, linolic acid, a linolenic acid, an elaidic acid, 2 ethylhexyl acid, or these fatty acids can be illustrated. What is necessary is to take into consideration the effectiveness of the product for which it asks in selection of these fatty acids, and just to decide suitably. If an environmental problem etc. is taken into consideration, the fatty acid of the natural animals-and-plants origin will be desirable, and if stability with the passage of time is desired, the fatty acid which does not have a partial saturation double bond two or more will be desirable. Moreover, if it says by fatty-acid chain length, carbon numbers 8-22 are desirable. If a desirable fatty acid is illustrated, it will be the mixture of oleic acid, a palmitic acid, a lauric acid, a capric acid, a caprylic acid, a ricinoleic acid, a condensation ricinoleic acid, a myristic acid, stearic acid, palmitoleic acid, behenic acid, or these fatty acids.

[0013] The polyglycerin and the fatty acid which are said to this invention are esterified by the well-known approach. For example, it can esterify under ordinary pressure or reduced pressure under an alkali catalyst, an acid catalyst, or a non-catalyst. Moreover, the charge of polyglycerin and a fatty acid must be suitably chosen for the purpose of a product. For example, what is necessary is just to make the mol number of fatty acids increase, if it is going to obtain an oleophilic surfactant that what is necessary is to calculate weight and just to teach so that it may become equimolar from the hydroxyl value of polyglycerin, and the molecular weight of a fatty acid by count, if it is going to obtain the surfactant of a hydrophilic property. The demand on use of a product may refine the obtained polyglyceryl fatty acid ester. What kind of well-known approach is especially sufficient as the approach of purification, and it is not limited. For example, by activated carbon, the activated clay, etc., and using an acid or alkali, it may wash, or molecular distillation may be performed [, and ], using a steam, nitrogen, etc. as carrier gas, you may refine, and carrying out separation removal etc. may carry out unreacted polyglycerin etc. using the liquid-liquid distribution, adsorbent, resin, molecular-sieving, loose reverse osmotic membrane, and ultra fill tray SHON film etc. [ carrying out adsorption treatment ] [ performing processing under reduced pressure ] Other components can be added to the polyglyceryl fatty acid ester of this invention, and the handling of a product can be made easy. For example, in order to reduce the viscosity of a product, kinds, such as ethanol, propylene glycol, a glycerol, polyglycerin, water, liquid sugar, and fats and oils, or two sorts or more may be added, and you may dissolve or emulsify. Or disintegration of the protein, such as polysaccharide, caseinate, etc., such as a lactose and a dextrin, may be added and carried out.

[0014] Depending on the purpose of use, the polyglyceryl fatty acid ester of this invention and other surfactants are mixed, and it is good also as surfactant pharmaceutical preparation. The surface active agent which can be used Lecithin or its partial hydrolysates, such as a soybean lecithin, yolk lecithin, and rapeseed lecithin, Caprylic-acid monoglyceride, capric-acid monoglyceride, lauric-acid monoglyceride, Myristic-acid monoglyceride, palmitic-acid monoglyceride, stearic acid monoglyceride, Behenic acid monoglyceride, oleic acid monoglyceride, elaidic-acid monoglyceride, Monoglyceride, such as ricinoleic-acid monoglyceride and condensation ricinoleic-acid monoglyceride, or such monoglyceride mixture, Or the acetic acid of these monoglyceride, a citric acid, a succinic acid, a malic acid, The organic-acid monoglyceride which is ester with organic acids, such as a tartaric acid, caprylic-acid sorbitan ester, Capric-acid sorbitan ester, lauric-acid sorbitan ester, myristic-acid sorbitan ester, Palmitic-acid sorbitan ester, stearic acid sorbitan ester, Behenic acid sorbitan ester, oleic acid sorbitan ester, elaidic-acid sorbitan ester, Sorbitan fatty acid esters, such as ricinoleic-acid sorbitan ester and condensation ricinoleic-acid sorbitan ester, Caprylic-acid propylene glycol ester, capric-acid propylene glycol ester, Lauric-acid propylene glycol ester, myristic-acid propylene glycol ester, Palmitic-acid propylene glycol ester, stearic acid propylene glycol ester, Behenic acid propylene glycol ester, oleic acid propylene glycol ester, Elaidic-acid propylene glycol ester, ricinoleic-acid propylene glycol ester, Propylene glycol fatty acid ester, such as condensation ricinoleic-acid propylene glycol ester, Caprylic-acid cane-sugar ester, capric-acid cane-sugar ester, lauric-acid cane-sugar ester, Myristic-acid cane-sugar ester, palmitic-acid cane-sugar ester, stearic acid cane-sugar ester, Behenic acid cane-sugar ester,

oleic acid cane-sugar ester, elaidic-acid cane-sugar ester, Sucrose fatty acid ester, such as ricinoleic-acid cane-sugar ester and condensation ricinoleic-acid cane-sugar ester, A soybean lecithin, yolk lecithin, or its enzyme decomposition product slack lysolecithin,